TOWARDS EXTREME ULTRAVIOLET TIME-RESOLVED LIQUID PHOTOELECTRON SPECTROSCOPY UTILIZING A HIGH-HARMONIC GENERATION PROBE SOURCE

ZACHARY N. HEIM, BLAKE A ERICKSON, ERICA LIU, DANIEL NEUMARK, *Department of Chemistry, The University of California, Berkeley, CA, USA*.

Time-resolved photoelectron spectroscopy (TRPES) has been used to study the ultrafast relaxation of electronically excited thymine, thymidine, and thymidine monophosphate on femtosecond time scales in liquid water. Pump-probe experiments have been carried out using tunable UV (4.7-5.2 eV) and 200 nm (6.2 eV) pulses, enabling the observation of relaxation dynamics of excited state populations from the $S_1(^1\pi\pi^*)$ excited state as well as a higher lying $S_n(^1\pi\pi^*)$ excited state. Relaxation lifetimes from the $S_1(^1\pi\pi^*)$ excited state have been obtained in reasonable agreement with previous work[a] and show no evidence of relaxation to the $S_2(^1n\pi^*)$ excited state, in contrast to transient absorption studies.[b,c] Additionally, relaxation from the higher lying $S_n(^1\pi\pi^*)$ excited state populated at 200 nm (6.2 eV) has been measured by TRPES for the first time and found to have a sub-picosecond lifetime. The current liquid TRPES experiment is unable to observe ground state population recovery subsequent to photoexcitation of these nucleic acid constituents due to insufficient probe energies. To remedy this deficiency, we are working to implement high-harmonic generation as a source of femtosecond XUV pulses capable of photoionizing solvated species with larger binding energies.

[a] Buchner, F.; Nakayama, A.; Yamazaki, S., et al., Journal of the American Chemical Society 2015, 137 (8), 2931-2938.

[b] Hare, P. M.; Crespo-Hernández, C. E.; Kohler, B., Proceedings of the National Academy of Sciences 2007, 104 (2), 435-440.

[c] Kwok, W.-M.; Ma, C.; Phillips, D. L., Journal of the American Chemical Society 2008, 130 (15), 5131-5139.